

THIRD ANNUAL SUMMARY REPORT

"DEVELOPMENT OF THERMALLY STABLE PHOSPHONITRILE
ELASTOMERS FOR ADVANCED AEROSPACE STRUCTURES"

Contract No. NAS8-25184

April 24, 1972 to June 24, 1973

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November 1973

to

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812



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TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
	Abstract	
1.0	Introduction and Summary	1
2.0	Experimental	5
2.1	Polymerization of Cyclic Phosphazene Oligomers	5
2.2	Preparation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Terpolymers	5
2.2.1	Preparation of the Terpolymer Using HCl Modified $[Cl_2PN]_n$	5
2.2.2	Preparation of a High Molecular Weight Terpolymer for a Coating Formulation	7
2.3	Fractionation Studies of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Terpolymers	9
2.3.1	Attempted Fractionation of a Terpolymer Oil and Elastomer	9
2.3.2	Fractionation of a Grease	11
2.4	Characterization Studies of Terpolymer Oil Fractions	12
2.4.1	Vapor-Liquid Phase Chromatography of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$	12
2.5	Attempted Determination of Hydroxyl Functionality	13
2.6	Room Temperature Solution Cure Studies of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-CH_3CH(OH)C_2H_4O_xPN]_n$ Terpolymers	15
2.7	Development of Room Temperature Moisture Cure of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$	15
2.7.1	Investigation of Isocyanate and Catalyst	15
2.7.2	Investigation of Solvent Systems	18

TABLE OF CONTENTS (continued)

<u>Section</u>		<u>Page</u>	
	2.7.3	Prepolymer Formation from [(CF ₃ CH ₂ O) ₂ PN-(C ₃ F ₇ CH ₂ O) ₂ PN- {CH ₃ CH(OH)C ₂ H ₄ O} _x PN] _n and BTDI	22
	2.7.4	Cured Film Studies	23
	2.7.5	Effect of Water on Cured Poly(fluoroalkoxyphosphazene)Films	24
	2.7.6	Dip Coating and Cure on a Circuit Board Substrate	25
	2.8	Directions for Preparation and Use of Curable Poly(fluorophosphazene) Coating	27
3.0	Discussion		28
	References		39
	Glossary		40
	Appendix		41

LIST OF TABLES

<u>Number</u>		<u>Page</u>
I	Polymerization of Cyclic Chlorophosphazenes	6
II	Characterization of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Terpolymers	8
III	Fractionation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Oil (1933-05T)	10
IV	Attempted Extraction of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Elastomers (1933-05)	11
V	Vapor-Liquid Chromatography of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$	13
VI	Reaction of 1,3-Butanediol with Arylisocyanates	14
VII	Attempted Room Temperature Solution Cures of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Terpolymers	16
VIII	Effect of Isocyanate and Catalyst on Moisture Curability and Shelf Stability	19
IX	Solvent Study for Curable Poly(fluorophosphazene)	21
X	Formation of Isocyanate Prepolymer as a Function of Time and % Total Solids	23
XI	Preparation of Cured Films	23
XII	Extraction of Cured Films	24
XIII	Study of Coating Variables on Film Thickness	26

ABSTRACT

Both high and low molecular weight, curable poly(fluoro-alkoxyphosphazene) terpolymers were prepared. These terpolymers resulted from reaction of $[\text{Cl}_2\text{PN}]_n$ polymer with an essentially equimolar amount of alkoxides derived from $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{C}_3\text{F}_7\text{CH}_2\text{OH}$ and a smaller amount of alkoxide derived from $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{OH}$. Both high and low molecular weight terpolymers were crosslinked with polyisocyanates at room temperature. Furthermore, high molecular weight materials were converted into isocyanate prepolymers which as films underwent moisture cures at room temperature. Prepolymer solutions were stable for several days. Aluminum and epoxy circuit boards were coated and the films showed good adhesion.

The effects of polymerization additives on the bulk polymerization of $(\text{Cl}_2\text{PN})_3$ were studied. Purified octachlorophosphazene, thiocyanate salts, or hydrogen chloride were employed in attempts to decrease molecular weight. Hydrogen chloride was found to be the most desirable agent for preparation of low molecular weight poly(dichlorophosphazene).

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"DEVELOPMENT OF THERMALLY STABLE PHOSPHONITRILE ELASTOMERS FOR ADVANCED AEROSPACE STRUCTURES"

1.0 INTRODUCTION AND SUMMARY

A research program to develop high strength, chemically resistant polymers which retain properties over a wide temperature range was begun several years ago at Horizons Incorporated. This research resulted in the preparation of poly(fluoroalkoxyphosphazene) elastomers and plastics which have a unique combination of properties [Ref. 1, 2]. These materials have very good low temperature properties and excellent solvent resistance. Programs were undertaken to compound and crosslink the $[(CF_3CH_2O)_2PN-(HCF_2C_3F_6CH_2O)_2PN]_n$ elastomer, and vulcanizates with tensile strengths of 1100-2200 psi, elongations of 100-350% and microhardness values of 30-90 units were obtained [Ref. 3, 4]. Furthermore, the vulcanizates had good resistance to jet fuels at elevated temperatures, excellent stability in various fluids, such as MIL H-5606, MIL L-7808, MIL L-23699, MIL H-83282, and MIL G-81322A(1) at temperatures ranging from 230-350°F. Vulcanizate properties undergo only minor changes when exposed for prolonged periods to boiling water.

The synthetic route to polyphosphazenes involves the preparation and subsequent reaction of soluble poly(dichlorophosphazene) as shown in Equations (1) and (2).



If mixtures of alkoxides are used, substitution occurs in a non-regular fashion and copolymers, terpolymers, etc., are obtained.

The objectives of this program conducted on Contract NAS8-25184 (April 24, 1972 to June 24, 1973) were to prepare poly(fluoroalkoxyphosphazenes) in a variety of molecular weight ranges and to crosslink these materials under mild conditions. The resultant sealants, potting compounds, coatings and elastomers are to be compatible with titanium and stable in the presence of fuels at 400-450°F. Also, the materials should have acceptable electrical and flame-retardant properties.

Earlier [Ref. 5], a high molecular weight poly(fluoroalkoxyphosphazene) elastomer was synthesized and crosslinked at room temperature. During this year's effort, the preparation of low molecular weight poly(dichlorophosphazene) was achieved. After derivatization of $[\text{Cl}_2\text{PN}]_n$ to form terpolymers, room temperature cures were accomplished by several methods. An epoxy substrate was coated with a high molecular weight terpolymer and cured by atmospheric moisture.

A variety of methods for the preparation of low molecular weight $[\text{Cl}_2\text{PN}]_n$ polymer were developed. Reproducibility of the polymerization was improved and relatively high yields of low molecular weight polymer were obtained.

Essentially two approaches were studied in an attempt to prepare low molecular weight poly(dichlorophosphazene) which after derivatization would be suitable for sealant, potting compound, or coating applications. In one approach, the purity of monomers employed in bulk polymerization was varied. Use of mixtures of purified or preferably unpurified, hexachlorophosphazene and octachlorophosphazene did afford substituted poly(fluoroalkoxyphosphazenes) which were greases and flowable gums. In another approach the effect of polymerization modifiers was investigated. Molecular weight was reduced by use of small quantities of HCl. Potassium thiocyanate was effective in giving low molecular weight $[\text{Cl}_2\text{PN}]_n$ polymer, but the derivatized product was obtained as a crosslinked material.

Both high and low molecular weight $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$ polymers which contained small amounts of the $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{O}-$ moiety were prepared and crosslinked at room temperature. Optimization of the concentration of terpolymer cure site was not undertaken, but the terpolymers were readily cured at room temperature by polyisocyanates in the presence of catalyst. Polymethylene polyphenyl isocyanate (PAPI) and bitolylene diisocyanate (BTDI), and dibutyltin diacetate catalyst were studied.

Furthermore, a high molecular weight $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}-\{\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{O}\}_x\text{PN}]_n$ terpolymer was converted into an isocyanate terminated prepolymer which cured at room temperature with atmospheric moisture. The formulated prepolymer solution had a shelf stability of several days.

The chemistry of the coating formulation was based on the catalyzed formation of isocyanate prepolymer by reaction of the terpolymer which contained hydroxyl functionality with excess equivalents of isocyanate reactant followed by atmospheric moisture curing of the resultant isocyanate-terminated prepolymers. Development of this system into a useable formulation for coating electrical circuit boards necessitated a study of variables such as solvent, polymer concentration, type of isocyanate, catalyst type and catalyst concentration, method of coating, and time interval between coats. The final formulation comprised a total solids content of 12.5% in Freon TA (azeotrope of $\text{CCl}_2\text{FCClF}_2$ and acetone), with BTDI as polyisocyanate and dibutyltin diacetate as catalyst. Films derived from this system were tack free in less than one hour and largely cured within three hours at room temperature. The cured films had low (6-7%) extractable content, good adhesion, and showed good qualitative resistance to hot water. No determination was made of thermal stability, titanium compatibility, or fuel resistance of the poly(fluoroalkoxyphosphazene) coating formulation.

2.0 EXPERIMENTAL

2.1 Polymerization of Cyclic Phosphazene Oligomers

The effect of monomer composition, purity, and the influence of several additives on the molecular weight and yield of $[\text{Cl}_2\text{PN}]_n$ was studied. Unless stated otherwise, polymerizations were conducted under vacuum with 50 g monomer in sealed Pyrex tubes. As received hexachlorophosphazene from El Monte Chemical Co. was reported to consist largely of $(\text{Cl}_2\text{PN})_3$ (70-80%) and $(\text{Cl}_2\text{PN})_4$ (20-30%) and was used after solution in benzene, filtration, and vacuum drying. When purified monomer was used, a distillation (b.p. 125-130°/10 mm Hg) and recrystallization (from *n*-heptane) were employed for purification. The results of these studies are given in Table I.

2.2 Preparation of $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}-\{\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{O}\}_x\text{PN}]_n$ Terpolymers

2.2.1 Preparation of the Terpolymer Using HCl Modified $[\text{Cl}_2\text{PN}]_n$

The $[\text{Cl}_2\text{PN}]_n$ polymer (35.8 g, 0.309 mole) from experiment 4 (Table I) was dissolved in 250 ml of dry benzene and was added over 1 hour to an alkoxide mixture prepared in 500 ml dry tetrahydrofuran from Na (14.6 g, 0.635 mole), $\text{CF}_3\text{CH}_2\text{OH}$ (24.7 g, 0.247 mole), $\text{C}_3\text{F}_7\text{CH}_2\text{OH}$ (49.4 g, 0.247 mole), and $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{OH}$ (22.2 g, 0.247 mole). The reaction was exothermic (55-60°C) and the mixture was heated at 66°C for an additional 16 hours. The cooled mixture (23°C) was acidified with 25 g of 10% HCl. Liquids were decanted from the white solids

TABLE I

Polymerization of Cyclic Chlorophosphazenes

Compound Number	Oligomeric (Cl ₂ PN) _n		Polymerization				[Cl ₂ PN] _n Polymer	
	n=	Purity	Additive	Amount (mole)	Time (hrs)	Temp. (°C)	[η]	Yield (%)
1742-28	3	distilled	-	-	6	270	-	45
1742-48	3,4	filtered	-	-	7	270	-	12
1850-26A	3,4	^a purified	-	-	6	270	0.70	23
1850-35	3,4	^a filtered	HCl	10 ⁻³	16	265	0.16	73
1959-08	3	purified	HCl	10 ⁻³	22.5	270	0.30	34
1959-16	3	purified	HCl	10 ⁻³	17 8	260 270	0.27	32
1850-46	3,4	^a filtered	CF ₃ SO ₃ H	10 ⁻³	2	270	very dark gelled	51
1959-03	3	purified	KSCN	0.043	8 7	200 250	gelled	77
1959-09	3	purified	KSCN	0.043	6.5	250	0.26	40
1850-47	3	purified	Hg(SCN) ₂	0.0047	24	250	very dark, but little heptane insolubles	
2001-02	3	distilled	-	-	17.3	270	-	50

^a 25 g each of purified trimer and tetramer

and combined with a 200 ml tetrahydrofuran rinse of the solids. Evaporation afforded, after water washing, an opaque, yellow-brown liquid (45.7 g, 46% yield) which was moderately viscous. The solids were washed twice with distilled water and then dissolved in 400 ml of Freon TA for additional washing. Precipitation with 2 volumes of n-heptane, followed by drying, gave a gray rubbery solid (24.7 g, 25% yield) with slow cold flow.

The liquid fraction was insoluble in ASTM Fuel A, but partly soluble in ASTM Fuel C, benzene, chloroform, methanol and n-heptane. The calculated mole % -OH of 27 from elemental analysis corresponds to an -OH content and functionality of 1.71 meq/g and 1.76, respectively. The liquid (1933-05T) and solid (1933-05) fractions were characterized by intrinsic viscosity, molecular weight and elemental analysis and the data are presented in Table II.

2.2.2 Preparation of a High Molecular Weight Terpolymer for a Coating Formulation

An alkoxide mixture was prepared by the reaction of $\text{CF}_3\text{CH}_2\text{OH}$ (350 g, 3.50 moles), $\text{C}_3\text{F}_7\text{CH}_2\text{OH}$ (700 g, 3.50 moles), and $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{OH}$ (180 g, 2.00 moles) with sodium (189.8 g, 8.25 moles) in 7.5 liters of dry tetrahydrofuran (THF). The alkoxide mixture was heated overnight at 48°C and the $[\text{Cl}_2\text{PN}]_n$ polymer/cyclic mixture (435 g, 7.50 equivs.), which had been prepared by polymerization of distilled $(\text{Cl}_2\text{PN})_3$ for 17.3 hours at 270°C,

TABLE II
Characterization of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-CH_3CH(OH)C_2H_4O]_xPN]_n$ Terpolymers

[Cl ₂ PN] _n Sample	Terpolymer Preparation	Physical State	Yield (%)	$[\eta]^{30^\circ C}$ Freon TF (dl/g)	Mole % ^a OH	M_{VPO}^b	Analysis (%)			
							C	H	N	Cl
1724-28	1782-29	rubbery solid	39	0.83	11.4	-	22.7	1.7	4.6	0.2
	1782-29T	oil	38	-	19.0	870	23.9	2.1	4.6	0.1
1742-48	1820-13	taffy like solid	28 ^c	0.12 ^d	-	-	-	-	-	-
	1820-13T	taffy like solid	28	0.06 ^d	38.2	2260	27.3	3.1	4.7	0.16
1850-26A	1880-45	rubbery solid	42	0.11	17.0	-	23.6	.1	5.1	0.05
	1880-45T	grease	29	0.03	32.0	2080	26.2	2.8	5.4	0.07
1850-35	1933-05	rubbery solid	25	0.3	15.0	2430 ^e	23.3	2.2	5.1	1.0
	1933-05T	visc. liquid	46	0.03	27.0	1030	25.2	2.4	5.0	1.8
1959-08	1933-34	rubbery solid	22	0.21	18.3	38000	23.8	2.2	-	0.17
	1933-34Rx	grease	41	0.04	33.3	1950	26.4	2.8	-	0.17
1959-16	2001-04	rubber	25	0.21	21.9	11200	24.4	2.3	-	0.04
	2001-04Rx	v. visc. liquid	36	0.04	33.3	1660	26.4	2.5	-	0.17
1959-09	1933-32	crosslinked	-	-	-	-	-	-	-	-
	1933-32Rx	v. visc. liquid	36	-	-	-	24.5	2.4	0.07 ^f	0.2
2001-02	2001-20RW	soft rubber	29	0.35	8.8	3848 ^g	22.3	1.6	-	0.2
	2001-20Rx	oil	57	-	28.9	840	25.5	2.1	-	0.04

^a Calculated from elemental analysis

^b Number average molecular weight by VPO in acetone

^c From 0.05 mole [Cl₂PN]_n

^d Freon TA as solvent

^e 5530 in Freon TF (CCl₂FCClF₂)

^f % sulfur

^g Sample used contained some residual NaCl, Freon TF used as solvent

was added as a benzene solution (2.7 liters) over 3 hours to the refluxing alkoxide solution. After addition was complete the reaction mixture was stirred at reflux (68°C) for 16 hours. The mixture at room temperature was acidified (pH 2) with 10% HCl and the clear yellow liquid decanted and combined with a 2 liter THF rinse of the solids. The solids were washed with 15 liters of water, dissolved in 3 liters of Freon TA, and washed exhaustively with water until the aqueous layer was free of chloride ion. The Freon TA solution was evaporated and dried to give a soft rubbery product (366 g, 29.4% yield). Data for the characterization of this whitish elastomer (2001-20RW) is presented in Table II. The calculated -OH content and functionality was 0.53 meq/g and 2.04, respectively.

The original decanted reaction liquor and THF rinse were evaporated, washed well with distilled water and dried to afford red-brown oil (2001-20Rx) (659 g, 57% yield) which is characterized in Table II. A solution of the above polymer (150 g) in Freon TA (1200 g) was supplied to NASA for evaluation as a coating for electrical circuit boards.

2.3 Fractionation Studies of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Terpolymers

2.3.1 Attempted Fractionation of A Terpolymer Oil and Elastomer

Terpolymer oil (10 g, 1933-05T) was extracted twice with 30 ml of n-heptane and the extracts were evaporated and dried to give fraction 1 (2.05 g) as a very fluid oil. The heptane insoluble residue was further extracted with benzene/

heptane (lv/lv, 30 ml). The benzene/heptane extract upon evaporation and drying gave fraction 2 (5.47 g) as a slightly more viscous oil than fraction 1, whereas the residue (fraction 3, 2.09 g) was a viscous oil. Fraction 3 was further extracted with benzene/heptane (lv/lv, 30 ml) to remove 0.46 g of clear yellow viscous oil. Characterization of the fractions are given in Table III.

TABLE III
Fractionation of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Oil
(1933-05T)

Fraction	Sample No.	Molecular Weights	$[\eta]^{30^\circ C}_{\text{acetone}}$ (dl/g)	Analysis (%) ^b	
				C	H
Untreated Oil	1933-05T	1030	0.03 (Freon TF)	25.2	2.4
1	1933-44H	942	-	24.6	2.2
2	1933-44H/B	984	-	24.9	2.5
3	1933-44	2190	0.04 (Freon TF)	23.1	1.9

^a VPO in acetone

^b Cl analysis found for untreated oil was 1.8%.

The soft, elastomer (5 g, 1933-05) was extracted three times with 30 ml portions of acetone. The combined extracts were evaporated and dried to give fraction 4 as a rubbery solid

(3.57 g) having very slow cold flow. The acetone insoluble residue was dried to give fraction 5 as a rubbery solid (1.46 g) having no cold flow. The two fractions are characterized in Table IV. Molecular weight by VPO could not be obtained due to insufficient solubility in suitable solvents.

TABLE IV

Attempted Extraction of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Elastomer
(1933-05)

Fraction (g)	$[\eta]_{\text{Freon TF}}^{30^\circ\text{C}}$ (dl/g)	Analysis (%)	
		C	H
4 (acetone soluble)	0.22	23.5	2.0
5 (acetone insoluble)	0.11	22.3	1.6

2.3.2 Fractionation of A Grease

The terpolymer grease (1.43 g, 1933-34-Rx) was mixed overnight with 10 ml of benzene/hexane (1v/1v) and the organic layer was evaporated to give fraction 6 as a mobil oil (0.66 g). The benzene/hexane insoluble residue was dried to give fraction 7 as a tacky elastomer (0.77 g). The oil fraction 6 was characterized by vapor-liquid phase chromatography as described in Section 2.4.1.

2.4 Characterization Studies of Terpolymer Oil Fractions

The purpose of these studies was to confirm the results indicated from the fractionation studies described in Section 2.3, namely, that the oil and grease fractions were composed of cyclic and linear specie. The $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ oil fractions (cf. fractions 1-3 of Table III), and the oil fractions from Section 2.3.2 were studied. Infrared studies of neat hydroxy containing fractions 1 and 3 and ultraviolet studies (3-5 mg per ml of spectro grade acetonitrile) of these same materials were inconclusive. A complete study of high molecular weight terpolymer was not attempted because this material showed poor solubility in the solvents employed for characterization studies of materials with lower molecular weights.

2.4.1 Vapor-Liquid Phase Chromatography of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$

Solutions (20% in acetone; Freon TA for elastomer 1880-45) of the oils were employed at 180°C using a 10% SE-30 on 80/100 mesh Supelco column and the data obtained are shown in Table V. Qualitatively comparable results were observed at both 160°C and 205°C.

TABLE V

Vapor-Liquid Chromatography of
 $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$

<u>Compound</u>	<u>Significant Volatile Components (excluding acetone)</u>
Fraction 1, Table III	2 pairs of relatively high boiling components
Fraction 2, Table III	1 pair of high boiling components, intermediate in retention to the pairs shown by Fraction 1
Fraction 3, Table III	Trace amounts of components shown in Fraction 2
Fraction 6, Section 2.3.2	3 high boiling components, corresponding to the majority of components in Fraction 2.
Terpolymer elastomer (1880-45)	None of the volatiles observed for hydroxy containing oils fractions 1, 2 or 6


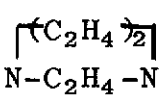
The presence of significant volatile components in the oil fractions and lack of these volatiles in the elastomer sample are taken as evidence for the presence of cyclic phosphazene components in the oil fractions.

2.5 Attempted Determination of Hydroxyl Functionality

A reliable determination of the OH content of the terpolymer was required. In preliminary studies a model compound and a variation of ASTM D1638-70 for the determination of -NCO content employed in polyurethane technology was investigated. Solutions (0.1 N) of 4-chlorophenylisocyanate, phenylisocyanate and di-n-butylamine were prepared in dry xylene. Solutions of

isocyanate (100% excess over OH) were added to a solution of 1,3-butanediol in xylene-tetrahydrofuran with and without catalyst (~10% on glycol). Aliquots of solution were removed, reacted with excess amine solution and titrated with standard 0.1 N HCl. In this manner the residual isocyanate could be determined. Assuming that the reacted isocyanate was equal to hydroxyl functionality consumed, the conversion of -OH was calculated. Table VI shows the effect of reaction variables on percent OH reacted.

TABLE VI
Reaction of 1,3-Butanediol with Arylisocyanates

R-  -NCO	Time (hrs)	Temperature (°C)	Catalyst	% OH Reacted
Cl	4	23	(C ₄ H ₉) ₂ Sn(C ₂ H ₃ O) ₂	8
Cl	4 1	23 79	(C ₄ H ₉) ₂ Sn(C ₂ H ₃ O) ₂	22
Cl	20 3	23 79		202
H	1-1/4	23	(C ₄ H ₉) ₂ Sn(C ₂ H ₃ O) ₂	59
H	17	23	(C ₄ H ₉) ₂ Sn(C ₂ H ₃ O) ₂	56

Greater than 100% conversion was found in one instance which indicated that the isocyanate reacted with something in addition to the glycol. A blank with isocyanate and catalyst at room temperature, in the absence of glycol, showed a drop in isocyanate activity. Presumably the catalyst effected addition reactions

of the isocyanate with itself and resultant loss of activity. This phenomenon has been reported [Ref. 7] for select combinations of polyfunctional isocyanates and catalysts. This investigation was abandoned due to time limitations.

2.6 Room Temperature Solution Cure Studies of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Terpolymers

Curing studies generally were carried out in closed vials by addition of polyisocyanate to the terpolymer solution (2-10 ml of tetrahydrofuran, Freon TA, or mixtures thereof) followed by addition of catalyst (DBTDA). After shaking well, samples were observed at regular time intervals. Three levels of polyisocyanate [50, 100, 150 mole % NCO relative to the calculated (from elemental analysis) mole % -OH in terpolymer] generally were employed. Results of these studies are shown in Table VII.

2.7 Development of Room Temperature Moisture Cure of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$

2.7.1 Investigation of Isocyanate and Catalyst

A solution of the terpolymer in dry Freon TA was treated with the polyisocyanate in tetrahydrofuran or acetone followed by catalyst (DBTDA) and mixed. Shelf stability of the mixture overnight and/or moisture curability of cast films were studied. Solubility as percent extractables was determined by shaking 2 days with 10 ml Freon TA, decanting and evaporating the liquor and vacuum drying the resultant residues. An excess of equivalents of isocyanate component was used, the quantity being

TABLE VII

Attempted Room Temperature Solution Cures of
 $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ Terpolymers

Terpolymer		Solvent	Isocya- nate	g	DBTDA Catalyst (μ l)	Time		Remarks
Sample	g					Hrs	Days	
1782-29	0.72	THF+	PAPI	0.018	15		1-3	loose gel
	0.72	Freon TA	PAPI	0.035	15		1-3	gel
	0.72		PAPI	0.07	15		1-3	tight gel
1782-29T	1.0	THF	TDI	0.04	4	168		no cure
	1.0	THF	TDI	0.09	9	64		precipitation of solid
	1.0	THF	TDI	0.13	13	168		precipitation of solid
	1.0	THF	PAPI	0.06	6	1/2		precipitation of solid
	1.0	THF	PAPI	0.13	13	1/2		precipitation of solid
	1.0	THF	PAPI	0.20	20	1/4		precipitation of solid
1820-13T	0.51	THF	PAPI	0.14	14		8	gel
	0.21	THF	PAPI	0.14	14		8	gel
	0.13	THF	PAPI	0.14	14		8	gel
1880-45T	0.80	THF	PAPI	0.06	20		1	precipitation of solid
	0.80	THF	PAPI	0.13	20		1	precipitation of solid
	0.80	THF	PAPI	0.20	20		1	precipitation of solid
	0.80	THF	PAPI	0.14	15		22	gel

TABLE VII (continued)

Terpolymer		Solvent	Isocya- nate	g	DBTDA Catalyst (<i>ul</i>)	Time		Remarks
Sample	g					Hrs	Days	
1933-05	0.53	THF+	PAPI	0.06	20	1		gel
	0.53	Freon TA	PAPI	0.10	20	1		opaque ^a
	0.53	"	PAPI	0.13	20	1		opaque ^a
1933-05T	0.80	none	PAPI	0.06	20		several	soluble
	0.80	none	PAPI	0.13	20		several	soluble
	0.80	none	PAPI	0.20	20		several	soluble
1933-34	0.88	THF+	PAPI	0.07	15		>3<16	gel
	0.88	Freon TA	PAPI	0.14	15		>3<16	gel
	0.88	"	PAPI	0.21	15		>3<16	opaque solution ^a
1933-34R	0.45	THF	PAPI	0.70	15		13	soluble
	0.45	THF	PAPI	0.21	15		13	soluble ^a
2001-04	0.72	THF+	PAPI	0.14	15		20	soluble
		Freon TA					24	loose gel
2001-04Rx	0.45	THF+ Freon TA	PAPI	0.14	15		20	loose gel

^a

Cured when film is cast from open dish

determined from the calculated mole % hydroxyl functionality in the terpolymer.

Before terpolymer sample 2001-20RW was treated in a fashion to completely remove salt (% Cl in terpolymer was 2.1), preliminary evaluations were conducted. This evaluation showed that the use of BTDI instead of PAPI or the use of DABCO instead of DBTDA gave better shelf stability but slightly higher % extractables. The results of these studies are shown in Table VIII and may be summarized as follows: (1) PAPI shows poorer shelf stability than TDI or BTDI, (2) a catalyst is necessary to minimize % Freon TA extractables, and (3) DBTDA offers the best compromise of low % extractables and shelf stability.

2.7.2 Investigation of Solvent System

Very preliminary solvent screening early in the program indicated that $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ terpolymer was quite soluble in Freon TA. Freon TA, however, exhibits high volatility and an attempt was made to minimize the evaporation rate of the developmental coating formulation by studying other solvents. Mixtures of terpolymer (1.0 g) and BTDI (0.14 g) were mixed with dry solvent(s) as shown in Table IX.

Samples 1, 2, 5, and 6 were very fluid but polymer settled from both after shaking and standing. Sample 7 did not dissolve polymer. Subsequent addition of catalyst (DBTDA, 6 mg)

TABLE VIII

Effect of Isocyanate and Catalyst on Moisture Curability and Shelf Stability

[(CF ₃ CH ₂ O) ₂ PN- (C ₃ F ₇ CH ₂ O) ₂ PN- {CH ₃ CH(OH)C ₂ H ₄ O} _x PN] _n							Remarks		
Sample	OH Content g (meq)	Used g (meq)	Iso- cyanate g (meq)	Freon TA (ml)	Co- solvent (ml)	Catalyst (g x 10 ²)	Shelf Stability of Solution	Film	% TA Extract.
1782-29	0.69	0.72 (0.5)	PAPI 0.19 (1.4)	5	THF (5)	-	fluid after 4 days	tacky, crumbly, insoluble	10 waxy solid
			"	5	"	DBTDA (1.5)	tight, springy gel after 4 days	tack free, relatively strong, insoluble	3 clear grease
			"	5	"	DABCO (1.5)	loose gel after 4 days	tack free, insoluble	2 clear grease
1782-29	0.69	0.72 (0.5)	TDI 0.09 (1.0)	5	"	-	fluid after 2 weeks	tacky, weak	19 waxy powder
			"	5	"	DBTDA (1.5)	fluid after 4 days, loose gel after 2 weeks	tack free, crumbly	5 waxy powder
			"	5	"	DABCO (1.5)	fluid after 4 days, loose gel after 6 days	tack free, strong	3 clear grease

TABLE VIII (continued)

$\begin{array}{l} [(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}- \\ (\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}- \\ \{\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{O}\}_x\text{PN}]_n \end{array}$		Iso- cyanate g (meq)	Freon TA (ml)	Co- solvent (ml)	Catalyst (g x 10 ²)	Remarks		
Sample	OH Content g (meq)	Used g (meq)				Shelf Stability of Solution	Film	% TA Extract.
2001-20RW		1.06 (0.56)	PAPI 0.188 (1.4)	3	Acetone (2.3)	DBTDA (0.6)	fluid with solid 5 days	tack free 6 greasy
		"	PAPI 0.234 (1.8)	3	"	"	"	tack free 8 greasy
		"	BTDI 0.148 (1.12)	4.8	-	"	fluid, 4 days	tack free 7 greasy

TABLE IX

Solvent Study for Curable Poly(fluoroalkoxyphosphazene)

Sample	% Total Solids of Mixture	Solvent (g) ^a						
		Freon TA (44)	Freon BF (48)	Acetone (56)	MEK (80)	Tri- chloro- ethylene (87)	Freon E-2 (104)	MIBK (116)
1	30	1.8	-	0.87	-	-	-	-
2	30	2.4	-	0.27	-	-	-	-
3	20	2.3	2.3	-	-	-	-	-
4	20	3.7	-	-	-	-	0.9	-
5	20	2.8	-	-	1.8	-	-	-
6	20	2.8	-	-	-	-	-	1.8
7	20	2.8	-	-	-	1.8	-	-
8	20	-	4.6	-	-	-	-	-

^a Boiling points (°C) are indicated in parentheses

in samples 5,6, and 7 led to increased opacity but not to solution of polymer. Films were cast onto aluminum from a vertical position using samples 3, 4, and 8. The film coat (1-2 mil) from 3 did not bubble but dried with many pinholes. The film coat (2-3 mils) from 4 when cast in a dish developed a marked surface pattern and bubbled extensively. Sample 3 gelled after 3 hours whereas 4 deposited some solid. The coated (1-2 mil) strip from 8 showed pronounced bubbling and pinholes. In conclusion, the above solvents were found to be less acceptable than Freon TA.

2.7.3 Prepolymer Formation from $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ and BTDI

Solutions of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ terpolymer (2001-20RW) had been formulated (see Section 2.6) with BTDI and DBTDA in Freon TA at 10, 15 and 17.5% total solids content. The conversion of -NCO was followed titrimetrically with time (ca. 23°C). The formulated polymer solution was diluted with 20 ml dry Freon TA and 10 ml of 0.25 N di(n-butylamine) in xylene was added. The solution was stirred for 5 minutes and excess amine titrated with 0.10 N HCl using bromophenol blue as indicator. The data obtained are shown in Table X, but the percent conversion is not corrected for possible oligomerization or polymerization reactions of isocyanate catalyzed by the DBTDA (see Section 2.5).

TABLE X

Formation of Isocyanate Prepolymer
As A Function of Time and % Total Solids

<u>% Total Solids of Solution</u>	<u>Reaction Time</u>	<u>% Conversion* of -OH</u>
10	6 days	108
15	6 days	50
17.5	3 hours	17
	24 hours	37
	48 hours	43

* uncorrected

2.7.4 Cured Film Studies

Solutions of the $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ terpolymer (1.06 g, 0.56 meq) were formulated as shown in Table XI and DBTDA catalyst (0.006 g) was added.

TABLE XI

Preparation of Cured Films

<u>Sample</u>	<u>PAPI (g)</u>	<u>BTDI (g)</u>	<u>Freon TA (g)</u>	<u>Acetone (g)</u>
1	0.188 (1.4 meq)	-	4.4	1.8
2	0.234 (1.75 meq)	-	4.4	1.8
3	-	0.148 (1.12 meq)	6.8	-

Films from each of the three samples were cast, allowed to air dry, vacuum dry (1 hour), and stirred with 10 ml of Freon TA for 2.5 days. The residue obtained from the Freon TA solution gave the % extractables shown in Table XII.

TABLE XII
Extraction of Cured Films

<u>Sample</u>	<u>Film Thickness (mils)</u>	<u>Air Drying Time (hrs.)</u>	<u>% Extractables ^a</u>	<u>Appearance of Extractables</u>
1	7.8 - 8.2	24	6.3	grease
2	6.5 - 7.5	24	7.6	grease
3	3.5 - 5.5	5 72	15.6 6.9	dry solid grease

^a from films of 0.084 - 0.175 g.

The unextracted air cured films (ca. 0.15 g) 2 and 3 were placed in vials containing 15 ml distilled water, heated 18 hours at 80°C and vacuum dried (3 hours). The films which showed no obvious change in texture or elasticity were extracted 2-1/2 days with 10 ml Freon TA. Both samples showed $6.5 \pm 0.2\%$ extractables in the form of a grease.

2.7.5 Effect of Water on Cured Poly(fluoroalkoxyphosphazene) Films

The effect of water immersion on typical BTDI and PAPI moisture cured poly(fluoroalkoxyphosphazene) films was determined at room temperature and at 80°C. Approximately 0.1 - 0.15 g films

were immersed in 10-15 ml of distilled water at 23-25°C and agitated for 3 days. Other samples were immersed in water which was maintained at 80°C for 18 hours. The samples treated at 25°C lost no weight upon vacuum drying. Treatment at 80°C showed no apparent change except for slight darkening. The heat treated samples were extracted with 10 ml Freon TA for 2-1/2 days and the % extractables determined. Both BTDI and PAPI cured polymers showed identical results, that is, $6.5 \pm 0.2\%$ extractables in the form of grease. This % extractable is similar to that obtained without water treatment and is probably due to low molecular weight species which lack or are low in hydroxyl content and therefore were not cured into the macromolecular matrix.

2.7.6 Dip Coating and Cure on a Circuit Board Substrate

A $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ terpolymer (2001-20RW) was dissolved in dry Freon TA. Pieces (9/16" x 1-3/4" x 1/16") of an epoxy circuit board supplied by NASA were scrubbed twice with Freon TA, soaked 5 minutes in Freon TA, and air dried. The effect on film thickness caused by coating method, % total solids (% TS) and interval between successive coats was studied and results are presented in Table XIII.

TABLE XIII
Study of Coating Variables on Film Thickness

Coating Method	Dipping ^a Interval (hrs.)	Film Thickness as Affected by % TS (mils)		
		10% TS	12.5% TS	15% TS
Open Container ^b	1/4	1	-	5
	3	1-1/4	-	6-1/2
Closed Container ^c	1/4	3/4	1	2
	3	1	1-1/2	3-1/2

^a Immersion time of 10 seconds for each of 2 dips

^b 1.5 liter beaker containing Freon TA covered tightly with aluminum foil

^c 5" x 5" x 3" stainless dish on its side

All coated films showed minute craters which appeared to be in the top coat. Prefiltration of the 12.5% TS formulation had little effect on the appearance of the final coating.

Film adhesion of the coated pieces obtained from the 12.5% TS formulation was made. The samples were cross-hatched with a razor blade, cellophane tape was pressed firmly over the

hatch marks, and the tape quickly pulled. All samples showed no adhesive film failure. These tested samples were recoated twice more (5-15 minute intervals) to give total film thicknesses of 3-1/4 to 4-1/4 mils and adhesion retested. No lifting of film was observed upon cross-hatching and tape pulling.

2.8 Directions for Preparation and Use of Curable Poly(fluoroalkoxyphosphazene) Coating

Given the data in Section 2.7, it seemed that optimum performance of the room temperature moisture curing $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ terpolymer could be achieved by use of Freon TA as solvent, BTDI as polyisocyanate, DBTDA as catalyst, and working at a total solids content of 12.5%.

A solution of terpolymer (2001-20RW, 150 g) in Freon TA (1200g) with smaller amounts of BTDA and DBTDA was supplied to NASA for evaluation as a coating for electrical circuit boards. A detailed description for the preparation and use of the room temperature curable poly(fluoroalkoxyphosphazene) is given in the Appendix.

3.0 DISCUSSION

Development of the poly(fluoroalkoxyphosphazenes) for sealant, potting or coating applications necessitates control of polymer molecular weight. In the past, high molecular weight $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ terpolymers which contained small amounts of -NH or -OH functionality were crosslinked with polyisocyanates at room temperature [Ref. 5]. In this year's effort, lower molecular weight $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]_n$ terpolymers which contained the $CH_3CH(OH)C_2H_4O-$ group were prepared and cured successfully. As with the earlier work, materials were obtained which ranged from fluid oils to elastomers. For the sake of clarity, the descriptive terms in this section of low, intermediate, and high molecular weight $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ terpolymer will be employed as follows: low will encompass fluid materials, intermediate will indicate grease or taffy-like solids, and high will designate elastomeric species.

The molecular weight values contained in this report as determined by vapor phase osmometry (VPO) should be viewed with considerable skepticism because this technique is used to determine, in solution, molecular weight values below 20,000. Higher molecular weight polymers require the use of other techniques. However, the physical properties of many of the poly(fluoroalkoxyphosphazene) materials prepared during this program did not correlate with the values obtained for their

molecular weight. Obvious differences in viscosity were not reflected by significant differences in VPO values. Presumably, the materials are mixtures which contain less and less low molecular weight specie as viscosity increases and as VPO sensitivity decreases.

Cure of the intermediate molecular weight terpolymers was achieved in solution using the taffy-like fraction derived from the polymerization of as received $(Cl_2PN)_3,4$ mixture. This material which had an intrinsic viscosity, $[\eta]$, of 0.06 dl/g (Freon TA, 30°C) was cured in solution at room temperature using PAPI and dibutyltin diacetate (DBTDA) as catalyst. The incompatibility of the terpolymer and PAPI necessitated the use of solvent to achieve homogeneity. Solventless formulations are preferred for sealant or potting applications. Attempted solventless cures of low molecular weight terpolymer ($[\eta] < 0.03$ dl/g, Freon TA, 30°C) using PAPI and DBTDA were unsuccessful, presumably due to insufficient crosslink density.

The sensitivity of crosslinking to stoichiometry and molecular weight of terpolymer was evidenced by absence of cure when the isocyanate equivalent per hydroxyl equivalent was raised from 100 to 150% (cf. Table VII, samples 1933-34), or when very low molecular weight material was employed. In the latter case, desirable properties probably would not have been obtained even if the product cured because of the high concentration of polyisocyanate required. Furthermore, the likely abundance of cyclic fluoroalkoxyphosphazenes also would be detrimental.

Molecular weight of the poly(fluoroalkoxyphosphazenes) probably is directly related to the molecular weight of the $[\text{Cl}_2\text{PN}]_n$ polymer and a limited investigation of molecular weight control was carried out. Earlier studies [Ref. 5] demonstrated molecular weight is reduced by various impurities which contain phosphorus-nitrogen bonds (octachlorophosphazene, etc.). Current molecular weight studies, with the exception of $(\text{Cl}_2\text{PN})_{3,4}$ mixtures, involved the effect of additives on the bulk polymerization of purified $(\text{Cl}_2\text{PN})_3$. The additives consisted of strong acids (HCl , $\text{CF}_3\text{SO}_3\text{H}$), and thiocyanate salts (K , Hg).

The most promising additive for reduction of molecular weight was hydrogen chloride. Despite an apparent retardation of polymerization rate (longer times at higher temperatures are required) in the presence of HCl , intrinsic viscosities of $[\text{Cl}_2\text{PN}]_n$ polymer of 0.16 and 0.27 dl/g (benzene, 30°C) were obtained from polymerizations conducted at 270°C with an as received $(\text{Cl}_2\text{PN})_{3,4}$ mixture and purified $(\text{Cl}_2\text{PN})_3$, respectively. A noteworthy feature of this very limited study was the improved reproducibility of polymerization and subsequent derivatization when purified $(\text{Cl}_2\text{PN})_3$ was polymerized at $265\text{--}270^\circ\text{C}$ in the presence of HCl . Percent conversion and intrinsic viscosity of $[\text{Cl}_2\text{PN}]_n$ polymers was excellent in duplicate runs. The derivatized terpolymers likewise showed remarkably good agreement with respect to the ratio of high and

low molecular weight fractions, intrinsic viscosity and mole % OH of these fractions. Reproducibility of larger scale bulk polymerizations was not investigated, but the size of the sample is known to affect polymerization time and yield.

This approach to formation of low molecular weight $[\text{Cl}_2\text{PN}]_n$ polymer appears more promising than previous studies by other workers [Ref. 8]. Their procedure consisted of dilute solution polymerization under pressure at 350°C in the presence of large amounts of HCl. When the amount of HCl was reduced, gelled polymer resulted.

Our success with HCl as a bulk polymerization modifier prompted the use of the stronger acid $\text{CF}_3\text{SO}_3\text{H}$. However, significant darkening and crosslinking were observed when an as received $(\text{Cl}_2\text{PN})_{3,4}$ mixture was polymerized at 270°C .

Polymerization of purified $(\text{Cl}_2\text{PN})_{3,4}$ 1:1 mixture afforded, after derivatization, an intermediate molecular weight terpolymer grease. Lastly, KSCN and $\text{Hg}(\text{SCN})_2$ were studied with purified $(\text{Cl}_2\text{PN})_3$. The monomer, $[(\text{SCN})_2\text{PN}]_3$, is known [Ref. 9] to polymerize, presumably, to $[(\text{SCN})_2\text{PN}]_n$ at 150°C . Partial replacement of Cl by NCS in $(\text{Cl}_2\text{PN})_3$ should create highly active sites and allow milder polymerization conditions which should afford lower molecular weight polymer. An in situ reaction of KSCN with molten $(\text{Cl}_2\text{PN})_3$ and concomitant polymerization were attempted. No apparent reaction occurred at 200°C , but conversion to 40% polymer was achieved by heating 6-1/2 hours at 250°C .

The intrinsic viscosity of polymer was 0.26 dl/g (benzene, 30°C) which appeared to lend some support to the above hypothesis. Unfortunately, subsequent derivatization afforded crosslinked terpolymer. Base catalyzed crosslinking via P-NCS sites may have occurred either during derivatization by polymerization or by reaction with hydroxybutyl groups. However, unexplained crosslinking during derivatization to poly(fluoroalkoxyphosphazene) copolymer of conventional $[\text{Cl}_2\text{PN}]_n$ has been observed infrequently in the past.

The $\text{Hg}(\text{SCN})_2$ catalyzed bulk polymerization was conducted at 150°C because the salt itself decomposes at 165°C. No polymer was obtained, perhaps because the polymerization temperature was too low.

In order to fully develop low molecular weight polymers curable at room temperature for potting and sealant applications, an understanding of the chemical composition of the various $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}-(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}-\{\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_4\text{O}\}_x\text{PN}]_n$ terpolymer fractions was desirable. The amount of cyclic specie and short chain linear materials in these fractions was unknown, but was expected to be variable. Cyclics could arise from incomplete purification of $[\text{Cl}_2\text{PN}]_n$ polymer-cyclic mixture or from degradation of poly(dichlorophosphazene) during derivatization. Cyclic species, if present, would affect curability and ultimate physical and chemical properties, but each specie should have a different volatility.

Gas chromatographic analysis of an oily terpolymer fraction (1933-44H/B) showed several volatile components which were presumed to be cyclic in nature. Solvent fractionation of an intermediate molecular weight terpolymer grease (1933-34-Rx) gave approximately equal amounts of an oil and a tacky elastomer. This oil was rich in volatile components as determined by gas chromatographic analysis. Several of the major volatile components appeared to be similar to those observed for the terpolymer oil (1933-44H/B).

The gas chromatographic data indicate the low and intermediate molecular weight terpolymers to be structurally heterogeneous. This mixture is comprised of cyclic species and polymeric species with the content of the latter increasing in progressing from low to intermediate molecular weight fractions.

The molecular weight as well as the amount of hydroxyl functionality are critical in the determination of the amount of crosslinking agent which is required to achieve cure of the terpolymers described in the report. Other methods, such as calculation from elemental analysis and nuclear magnetic resonance, which we employed, have not given satisfactory agreement among themselves.

Development of a reliable determination for the OH content using model compounds and a variation of ASTM D1638-70 for the determination of -NCO content in polyurethane technology was attempted. Compounds employed were phenyl and 4-chlorophenyl

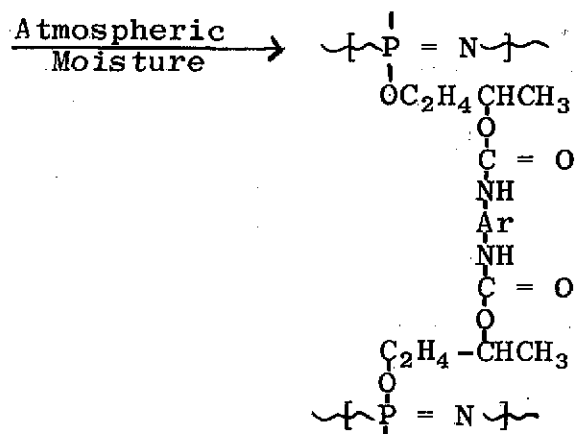
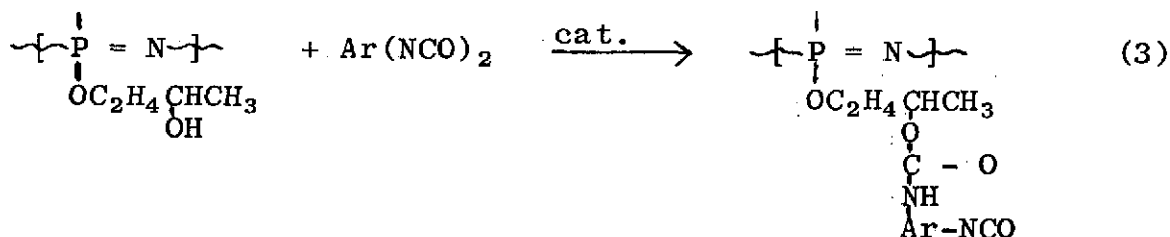
isocyanates and 1,3-butanediol, whereas DBTDA and DABCO were used as catalysts under various reaction conditions. The percent hydroxyl reaction was monitored titrimetrically. Greater than 100 percent conversion was found in one instance which indicated that the isocyanate reacted with something in addition to the glycol. A blank run with isocyanate and catalyst at room temperature, in the absence of glycol, showed a drop in isocyanate activity. Presumably, the catalyst effected addition reactions of the isocyanate with resultant loss of activity. This phenomenon has been reported [Ref. 7] for select combinations of polyfunctional isocyanates and catalysts. This study was discontinued.

Attempts to crosslink poly(fluoroalkoxyphosphazene) terpolymers in the absence of solvent were unsuccessful due to the incompatibility of the poly(fluoroalkoxyphosphazene) terpolymer oils with the hydrocarbon isocyanates studied. Presumably, the use of fluorinated isocyanates would eliminate the compatibility problem and miscible mixtures with the poly(fluoroalkoxyphosphazene) terpolymers could be prepared.

Since NASA has a need for a coating system (which could be solvent based) for electrical components, high molecular weight poly(fluoroalkoxyphosphazene) coatings were investigated. These coatings must have good electrical properties, minimum shrinkage, adhesion, abrasion resistance and environmental resistance and environmental resistance were required. Ideally,

the coating system would be a 1-package formulation stable indefinitely at relatively high solids content (30-50%) and would afford uniform cured films preferably upon standing at room temperature (but no greater than 80°C).

The approach to obtain such a useable coating involved converting a high molecular weight hydroxyl containing poly(fluoroalkoxyphosphazene) into an isocyanate prepolymer which would cure at room temperature. Similar chemistry has been employed for moisture curing polyurethane coatings. In this manner poly(fluoroalkoxyphosphazene) coatings which were tack free in less than one hour, and largely cured within three hours, were obtained. The isocyanate prepolymers were prepared by reaction of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ with excess equivalents of polyisocyanate. Applicable reactions are shown in Equation (3).



where Ar = a divalent aromatic radical

The polyfunctionality of both the $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ terpolymer and the polyisocyanate necessary for prepolymer formation precluded development of an indefinitely stable 1-package system. Furthermore, the high molecular weight of the poly(fluoroalkoxyphosphazene) prevented a useable, high-solids formulation. However, a compromise was achieved by development of a multi-package system which had 3-4 days shelf life after mixing of the components which utilized 12.5% total solids content.

Some of the variables that were studied during the development of this two part system included determination of suitable solvent, polyisocyanate, percent total solids content, catalyst, method of dip coating, and time between successive dip coats, if desired. Two polyisocyanates were considered for the preparation of the isocyanate terminated prepolymers, namely, BTDI and PAPI. The 2,4-toluene diisocyanate (TDI) was not considered except for early screening purposes because of its relatively high vapor pressure and attendant toxicity problems. BTDI was chosen over PAPI because it was more soluble in Freon TA, afforded greater shelf stability of final product, and gave less color in the coating.

Due to the limited solubility of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN]-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ in common organic solvents, a strong

limitation was placed on the solvent carrier for the coating formulation. The terpolymer is readily soluble in Freon TA (b.p. 44°C) or Freon TA-acetone mixtures. However, the low boiling point and hence rapid evaporation rates of these solvents led to extensive pin-holing and cratering at total solids content as low as 15%. Film defects were minimized by using formulations at 10-12.5% total solids content. In attempts to raise the boiling point of the carrier, higher boiling solvents such as methyl ethyl ketone (b.p. 80°C), Freon E-2 (b.p. 104°C), methyl isobutyl ketone (b.p. 116°C), or trichloroethylene (b.p. 87°C) were investigated. However, the terpolymer was either insoluble or separated upon standing in these solvents.

Selection of catalyst involved a cursory examination of DBTDA, a catalyst used in earlier solution room temperature cure studies, and 1,4-diazabicyclo[2.2.2]octane (DABCO). Tin salts and tertiary amines are extensively used in polyurethane technology. Greater solution stability for TDI based prepolymers was observed with DBTDA over DABCO while PAPI based prepolymers gave stronger air cured films with DBTDA.

These studies led to the selection of BTDI as polyisocyanate, DBTDA as catalyst, and Freon TA as solvent for the final coating formulation. Consideration now had to be devoted to film thickness and method of application. Film thickness

was found to be dependent on percent total solids content, time interval between coats and method of coating (open vs closed chamber). Increased film thicknesses were obtained by an increase in percent total solids content and an increase in time interval between coats, and by utilization of a relatively open coating chamber. A solids content of 12.5% appeared to offer a balance in final film thickness and film appearance. At this concentration, films of 1.5 mils could be obtained by a 2-dip coating process. The films showed low extractables content (6-7% using Freon TA), good adhesion (cross hatch test), and good resistance to hot water (18 hours at 80°C). Samples of this formulation will be tested for utility in electrical applications at NASA (Marshall Space Flight Center, S+E-ASTN-MNP).

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GLOSSARY

Solvents:

Freon TA	89% $\text{CClF}_2\text{CCl}_2\text{F}$ /11% CH_3COCH_3 (duPont)
Freon TF	$\text{CClF}_2\text{CCl}_2\text{F}$ (duPont)
THF	Tetrahydrofuran

$[\eta]$ Intrinsic viscosity, dl/g

Isocyanates:

PAPI Polymethylene polyphenylisocyanate
(2.8 NCO/mole) (Upjohn)

TDI Toluene diisocyanate (2,4 isomer)

ETDI Bitolylene diisocyanate (Upjohn)

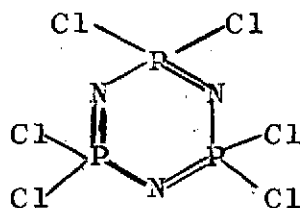
Catalysts:

DBTDA Dibutyltin diacetate

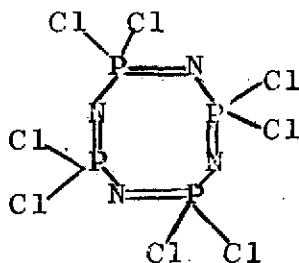
DABCO 1,4-diazabicyclo[2.2.2]octane (triethylene diamine)

VPO Vapor pressure osmometry

$(\text{Cl}_2\text{PN})_3$



$(\text{Cl}_2\text{PN})_4$



APPENDIX

DIRECTIONS FOR COATING OBJECTS WITH ROOM TEMPERATURE CURABLE POLY(FLUOROALKOXYPHOSPHAZENES)

CAUTION: THESE MATERIALS REQUIRE MOISTURE
TO CROSSLINK. KEEP CONTAINERS
CLOSED FOR BEST SHELF-LIFE.

The coating solution is prepared from 10.0 parts by weight of polymer in solution, 1.40 parts by weight of diisocyanate, and 0.175 parts by weight of catalyst.

Formulation consists of:

Step 1 Add diisocyanate to the polymer solution and
 mix well (1/2 to 1 hour) in a closed container.

Step 2 Add catalyst and mix in a closed container for
 16-20 hours at room temperature.

The solution (12.5% total solids content) will become opaque white and is ready for use, but must be stored at 75°F or less and must be used within two days.

Step 3 Immerse the thoroughly cleaned and dried object
 to be coated into the above formulation for
 10 seconds.

Step 4 Immediately after dipping, transfer the object
 to a chamber which has been presaturated (allow
 1/2 hour) with dry Freon TA (see Figure 1).

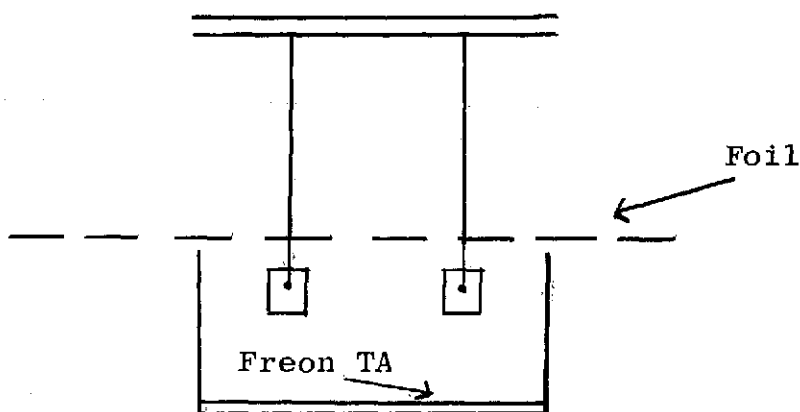


FIGURE 1

Step 5 Additional coats may be applied by redipping the object in the formulation after no less than five minutes and no more than 1 day (but preferably 15-30 minutes).

Approximate film thickness will be 1 mil per coat. Thinner coats (0.6 mil) may be obtained by dipping at 5 minute intervals.

Curing consists of:

The coated object should be allowed to stand in air (moist) at room temperature for at least one day.

The coating formulation is composed of, or a fraction thereof,

Polymer solution

100 parts of $[(CF_3CH_2O)_2PN-(C_3F_7CH_2O)_2PN-\{CH_3CH(OH)C_2H_4O\}_xPN]_n$ in 800 parts Freon TA

Diisocyanate

bitolylene diisocyanate (Upjohn Co.)

Catalyst

dibutyltin diacetate